

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of:

ARCELLA et al

Group Art Unit: Not yet assigned

Serial No.: New Application

Examiner: Not yet assigned

Filed: February 25, 2002

Attorney Dkt. No.: 108910-00053

For: POROUS HYDROPHILIC MEMBRANES

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

February 25, 2002

Sir:

Prior to calculation of the filing fees and initial examination of the application, please amend the above-identified application as follows:

IN THE CLAIMS:

Please amend claims 3-6, 9-15, 17-19 and 21-23 as follows. A copy of the marked up original claims is attached to this response showing the changes as set forth in amended 37 CFR 1.121.

3. (Amended) Membranes having pores totally occluded to gases according to claim 1, containing an ionomer amount higher than about 30% by weight.

4. (Amended) Membranes having pores partially occluded to gases according to claim 1, containing an ionomer amount lower than about 20% by weight.

5. (Amended) Membranes according to claim 1, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.

6. (Amended) Membranes according to claim 1, wherein the ionomers are (per)fluorinated polymers and they preferably have SO₃H and/or -COOH, preferably SO₃H, functionality, and an equivalent weight such as to result amorphous.

9. (Amended) Membranes according to claim 7, wherein the fluorinated monomers of type (B) are selected from the following:

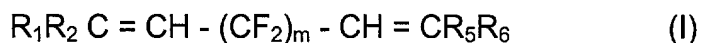
- F₂C=CF-O-CF₂-CF₂-SO₂F;
- F₂C=CF-O-[CF₂-CXF-O]_n-CF₂-CF₂-SO₂F

wherein X = Cl, F or CF₃; n = 1-10;

- F₂C=CF-O-CF₂-CF₂-CF₂-SO₂F
- F₂C=CF-Ar-SO₂F wherein Ar is an aryl ring;
- F₂C=CF-O-CF₂-CF₂-CF₂-COF
- F₂C=CF-O-[CF₂-CXF-O]_n-CF₂-CFX-COF

wherein X = Cl, F or CF₃; n = 1-10.

10. (Amended) Membranes according to claim 1, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:



wherein:

m = 2-10, preferably 4-8;

R₁, R₂, R₅, R₆, equal to or different from each other, are H or C₁ - C₅ alkyl groups.

11. (Amended) Membranes according to claim 1, wherein the ionomers comprise:

- monomeric units deriving from TFE;
- monomeric units deriving from CF₂=CF-O-CF₂CF₂SO₂F;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. (Amended) Membranes according to claim 1, wherein the amorphous ionomer shows a substantial absence of crystallinity.

13. (Amended) Membranes according to claim 1, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.

14. (Amended) Membranes according to claim 1, wherein the (per)fluorinated ionomers are crosslinked.

15. (Amended) Membranes according to claim 1, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

17. (Amended) Use of the membranes according to claim 1 in separation processes, preferably in microfiltration and ultrafiltration processes of aqueous solutions, and in pervaporation processes.

18. (Amended) Use according to claim 17, wherein the membranes have pores partially or totally occluded to gases, and contain an ionomer amount higher than about 30% by weight, and are used in iperfiltration and reverse osmosis processes.

19. (Amended) A process for preparing hydrophilic porous membranes according to claim 1, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing hydrophilic groups, preferably having $-SO_3H$ or $-COOH$ functionality, said process comprising the following steps:

- a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolysable groups, preferably $-SO_2F$, $-COOR$, $-COF$, wherein R is a C_1 - C_{20} alkyl radical or a C_6 - C_{20} aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight till obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures comprised between the room temperature and $120^\circ C$, preferably between $15^\circ C$ and $40^\circ C$; the so impregnated membrane is subjected to thermal treatment at temperatures from 50° to $200^\circ C$, preferably from 120° to $160^\circ C$ till substantial removal of the solvent and

obtainment of a substantially transparent membrane, optionally step a) is repeated until the membrane appears substantially transparent;

- b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkali, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from $-\text{SO}_2\text{F}$ into $-\text{SO}_3^-$, and of the $-\text{COOR}$, $-\text{COF}$ groups into $-\text{COO}^-$ groups;
- c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;
- d) optionally treatment with water at temperatures in the range 50°C - 100°C , in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.

21. (Amended) A process according to claim 19, wherein in step b) the used strong alkalis are the hydroxides of the Group Ia metals.

22. (Amended) A process according to claim 19, wherein at the end of step b) washings with water are carried out until a neutral pH of the washing waters is obtained.

23. (Amended) A process according to claim 19, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.

REMARKS

Claims 1-24 are pending in this application. By this Amendment, claims 3-6, 9-15, 17-19 and 21-23 are amended to correct the multiple dependency thereof and to place this application into better condition for examination. No new matter has been added.

In the event that there are any fees due with respect to the filing of this paper, please charge Deposit Account No. 01-2300.

Respectfully submitted,



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Enclosures: Marked-up Copy of Amended Claims

MARKED-UP COPY OF AMENDED CLAIMS
ATTY. DOCKET NO. 108910-00053

3. (Amended) Membranes having pores totally occluded to gases according to [claims 1-2] claim 1, containing an ionomer amount higher than about 30% by weight.

4. (Amended) Membranes having pores partially occluded to gases according to [claims 1-2] claim 1, containing an ionomer amount lower than about 20% by weight.

5. (Amended) Membranes according to [claims 1-4] claim 1, wherein the porous support is formed by (per)fluoropolymers, preferably PTFE, still more preferably bistretched PTFE.

6. (Amended) Membranes according to [claims 1-5] claim 1, wherein the ionomers are (per)fluorinated polymers and they preferably have SO₃H and/or -COOH, preferably SO₃H, functionality, and an [equivalent] equivalent weight such as to result amorphous.

9. (Amended) Membranes according to [claims 7-8] claim 7, wherein the fluorinated monomers of type (B) are selected from the following:

- F₂C=CF-O-CF₂-CF₂-SO₂F;
- F₂C=CF-O-[CF₂-CXF-O]_n-CF₂-CF₂-SO₂F

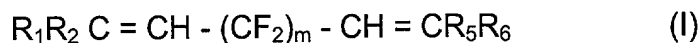
wherein X = Cl, F or CF₃; n = 1-10;

- F₂C=CF-O-CF₂-CF₂-CF₂-SO₂F

- $F_2C=CF-Ar-SO_2F$ wherein Ar is an aryl ring;
- $F_2C=CF-O-CF_2-CF_2-CF_2-COF$
- $F_2C=CF-O-[CF_2-CXF-O]_n-CF_2-CFX-COF$

wherein X = Cl, F or CF_3 ; n = 1-10.

10. (Amended) Membranes according to [claims 1-9] claim 1, wherein the ionomers contain from 0.01 to 5% by moles of monomeric units deriving from a bis-olefin of formula:



wherein:

m = 2-10, preferably 4-8;

R_1, R_2, R_5, R_6 , equal to or different from each other, are H or $C_1 - C_5$ alkyl groups.

11. (Amended) Membranes according to [claims 1-10] claim 1, wherein the ionomers comprise:

- monomeric units deriving from TFE;
- monomeric units deriving from $CF_2=CF-O-CF_2CF_2SO_2F$;
- monomeric units deriving from the bis-olefin of formula (I);
- iodine atoms in end position.

12. (Amended) Membranes according to [claims 1-11] claim 1, wherein the amorphous ionomer shows a substantial absence of crystallinity.

13. (Amended) Membranes according to [claims 1-11] claim 1, wherein the amorphous ionomer has a residual crystallinity lower than 5%, preferably lower than 1%.

14. (Amended) Membranes according to [claims 1-13] claim 1, wherein the (per)fluorinated ionomers are crosslinked.

15. (Amended) Membranes according to [claims 1-13] claim 1, containing one or more amorphous or crystalline (per)fluoropolymers, the amorphous ones being different from the ionomer used in the membrane.

17. (Amended) Use of the membranes according to [claims 1-16] claim 1 in separation processes, preferably in microfiltration and ultrafiltration processes of aqueous solutions, and in pervaporation processes.

18. (Amended) Use according to claim 17, wherein the membranes [are those of claim 3] have pores partially or totally occluded to gases, and contain an ionomer amount higher than about 30% by weight, and are used in iperfiltration and reverse osmosis processes.

19. (Amended) A process for preparing hydrophilic porous membranes according to [claims 1-16] claim 1, comprising a porous support formed by a (per)fluorinated polymer, and amorphous (per)fluorinated ionomers containing

hydrophilic groups, preferably having $-\text{SO}_3\text{H}$ or $-\text{COOH}$ functionality, said process comprising the following steps:

- a) impregnation of the porous support formed by the (per)fluorinated polymer, with a (per)fluorinated ionomer having hydrolysable groups, preferably $-\text{SO}_2\text{F}$, $-\text{COOR}$, $-\text{COF}$, wherein R is a $\text{C}_1\text{-C}_{20}$ alkyl radical or a $\text{C}_6\text{-C}_{20}$ aryl radical, using a solution of the ionomeric compound in fluorinated organic solvent at a concentration in the range 1-20% by weight, preferably 4-20% by weight till obtaining a membrane having the pores substantially filled by the ionomeric solution, the impregnation is carried out at temperatures comprised between the room temperature and 120°C , preferably between 15°C and 40°C ; the so impregnated membrane is subjected to thermal treatment at temperatures from 50° to 200°C , preferably from 120° to 160°C till substantial removal of the solvent and obtainment of a substantially transparent membrane, optionally step a) is repeated until the membrane appears substantially transparent;
- b) treatment of the membrane obtained in a) with inorganic strong, preferably aqueous, alkali, i.e. bases which are completely dissociated in water, to obtain the conversion of the functional groups into hydrophilic groups, preferably from $-\text{SO}_2\text{F}$ into $-\text{SO}_3^-$, and of the $-\text{COOR}$, $-\text{COF}$ groups into $-\text{COO}^-$ groups;
- c) treatment of the membrane obtained in b) with inorganic strong acids, i.e. acids which are completely dissociated in aqueous solution, obtaining the (per)fluorinated ionomer in acid hydrophilic form;

- d) optionally treatment with water at temperatures in the range 50°C - 100°C, in case repeated, until removal of the ionomer in excess and neutral pH of the washing waters.

21. (Amended) A process according to [claims 19-20] claim 19, wherein in step b) the used strong alkalis are the hydroxides of the Group Ia metals.

22. (Amended) A process according to [claims 19-21] claim 19, wherein at the end of step b) washings with water are carried out until a neutral pH of the washing waters is obtained.

23. (Amended) A process according to [claims 19-22] claim 19, wherein the ionomer is crosslinked by adding to the impregnation solution a) crosslinking agents.